Synthesis of scandia-stabilized zirconia nanoparticles by the polyacrylamide technique

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Abstract

The synthesis of ZrO_2:10 mol% Sc_2O_3 powders by the polyacrylamide technique was carried out using zirconium and scandium precursor solutions, acrylamide, N,N'-methylene-bisacrylamide and ammonium persulfate. The polymerization process occurred in few seconds and, without any precipitation, transparent polymeric gels were obtained. Calcination of the gels produced nanosized ceramic powders fully stabilized in the cubic fluorite structure. High specific surface area powders of 78 m^2/g, corresponding to ~13 nm average particle size for an average crystallite size of 5 nm, evaluated by X-ray diffraction, were obtained after calcination at 500 °C. The powders were characterized by *in situ* high temperature X-ray diffraction and scanning electron microscopy. Pellets sintered at 1500 °C show high values of oxide ion conductivity.
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1. Introduction

Solid electrolytes based on solid solutions of zirconium oxide with aliovalent cation oxides (Y_2O_3, MgO, CaO, Sc_2O_3) have been developed for applications in electrochemical devices such as solid oxide fuel cells (SOFCs), oxygen sensors and catalytic membrane reactors due to their electrical properties [1,2]. The main effect of the introduction of aliovalent cations in the zirconium oxide lattice is the creation of oxide ion vacancies, which are the charge carriers for enhanced ionic conductivity. Moreover, in these defective oxides the high temperature cubic phase becomes stable at room temperature. Among these compounds, scandia-stabilized zirconia (ZrO_2: Sc_2O_3 – ScSZ) shows the highest value of electrical conductivity in the electrolytic region. This has been attributed to the low association enthalpy of the defect reactions and the similarity between the Sc^{3+} and Zr^{4+} ionic radii [3]. Therefore, this also means that for the same ionic conductivity value of yttria-stabilized zirconia electrolytes (ZrO_2:Y_2O_3 – YSZ), the

working temperature of SOFCs with ScSZ electrolytes can be lowered by about 100 K [4]. Several routes have been exploited to develop electrolytes with high performance for the fabrication of SOFCs with high-energy-converting efficiency and extended operating lifetime. Synthesis by the solid state route usually yields uncontrolled crystallite growth, which could induce chemical and grain size non-uniformity [5].

Synthesis using chemical routes have many advantages for the fabrication of components for SOFCs, particularly because mixing of the reagents occurs at the molecular level in solution, resulting in a product with very high homogeneity. Different chemical routes have been reported to obtain fine ceramic powders of ScSZ, such as sol–gel [1], co-precipitation [4,6,8], glycine nitrate process [7], citrate process [8], polymeric precursor technique [9], spray drying [10], and combustion route [11]. These techniques are time consuming if large quantities of fine powders are required.

The polyacrylamide sol–gel process is a fast, non-expensive, reproducible, and easily scale up chemical route for obtaining fine powders of oxides at a reasonable rate. It has already been proposed to synthesize fine powders of $2SiO_2$–$3Al_2O_3$ (mullite), $LaAlO_3$ [12], Y-123 ($YBa_2Cu_3O_7$) [12,13], $La_{1.85}Sr_{0.15}CuO_4$

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[14], $Hg_{1-x}Re_xBa_2Ca_2Cu_3O_{8+x}$ [15], $BaZrO_3$ [16], and $La_{1-x}MnO_{3\pm\delta}$ [17]. Some chemical syntheses of ceramic powders produce solutions that when stored are usually sensitive to ambient conditions like atmosphere, temperature, humidity and light exposure. One of the main advantages of the polyacrylamide technique is that the powders may be stored in a highly stable gel form. Gels here prepared were kept stored in a transparent plastic container in contact with atmospheric air without any degradation.

In this study, ScSZ powders of with 10 mol% Sc_2O_3 were prepared by the polyacrylamide technique [5]. Furthermore, ScSZ was also prepared by the polymeric precursor technique for comparison of the properties of powders synthesized by both techniques.

2. Experimental

The starting materials were zirconium hydroxide, $Zr(OH)_4 \cdot nH_2O$ (produced at this Institute), scandium oxide (Sc_2O_3, 99,9%, Aldrich), citric acid ($C_6H_8O_7$, 99.5%, Synth), nitric acid (HNO_3, 65%, Vetec), ethylene glycol (CH_2OHCH_2OH, 99%, Synth), acrylamide (C_3H_5NO, 98%, Vetec), N,N'-methylenebisacrylamide ($C_7H_{10}N_2O_2$, 98%, Vetec) and ammonium persulfate (($NH_4)_2S_2O_8$, 98%, Vetec). $Zr(OH)_4 \cdot nH_2O$ and Sc_2O_3 were first dissolved separately in a hot nitric acid solution under stirring. After their dissolution, the Zr^{4+} and Sc^{3+} cations (M^{x+}) were complexed by the addition of citric acid (CA) in the 1:1.2 ratio and the pH was adjusted (3 to 5) just to dissolve completely the species into a clear solution. Afterwards, the stock solutions were mixed in the molar ratios $(0.90)Zr^{4+}:(0.10)$ Sc^{3+} to obtain the precursor solution. Details of the chemical steps for the polyacrylamide and the polymeric precursor techniques will be described elsewhere [18].

After calcination, the powders were analyzed by laser scattering (1064, Cilas), gas adsorption (BET method, ASAP 2000, Micromeritics), scanning electron microscopy (XL 30, Philips) and *in situ* high temperature (up to 900 °C) X-ray diffraction (D8 Advance-Bruker-AXS, Anton Paar HTK1400 sample chamber, Braun PSD detector). The powders were pressed to pellets and sintered at 1500 °C. The apparent density was evaluated by the Archimedes method resulting in 5.06 and 5.38 g/cm^3 using powders synthesized by the Pechini technique and the polyacrylamide technique, respectively. The sintered pellets were analyzed by X-ray diffraction in a θ–2θ Bragg–Brentano configuration at 40 kV–40 mA with Cukα radiation, in the 20°–40° 2θ range. Average crystallite sizes D were calculated with the Scherrer equation. Impedance spectroscopy measurements were carried out in the temperature range 300–400 °C with a Hewlett Packard 4192A LF Impedance Analyzer in the 5 Hz–13 MHz range in pellets with silver electrodes. A special software was used for collecting and analyzing the $[-Z''(\omega) \times Z'(\omega)]$ impedance data [19].

3. Results and discussion

Strong evidences on modification of the powders during calcination are the values of the specific surface area. Both powders prepared according to the two different routes have high surface area (78 m^2/g and 167 m^2/g for powders synthesized by the polyacrylamide technique and by the polymeric precursor technique, respectively, after calcination at 500 °C), which decreases for increasing calcination temperature due to agglomeration provided by the increase in energy during the combustion of organic compounds. An estimate of the value of the average particle size was done resulting in 13 nm and 6 nm for powders prepared by the polyacrylamide technique and by the polymeric precursor technique, respectively, in agreement with the average crystallite size (see below), showing that the nanosized particles are single crystalline.

Fig. 1 shows high temperature powder diffraction patterns of zirconia-10 mol% scandia powders synthesized by the polyacrylamide and the polymeric precursor techniques. While the powders synthesized by the former technique have a set of peaks related only to the fluorite cubic phase, for the powder synthesized by the latter technique the monoclinic phase is also present.

Analysis by scanning electron microscopy of the as-synthesized ZrO_2:10 mol% Sc_2O_3 powders show that powders obtained by the polymeric precursor technique consist mainly of small hard agglomerates or grains of diameter around 20 μm, exhibiting irregular shapes with faceted borders, often lengthened. However, these grains in fact consist of nanoparticles that are sintered in the high-energy environment during the thermal decomposition of high quantities of organic compounds used in the synthetic route. The powders obtained by the polyacrylamide technique, on the other hand, consist mainly of small soft
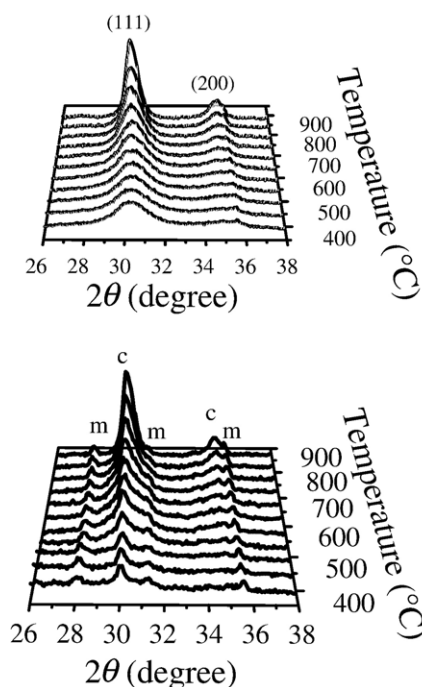

Fig. 1. High temperature X-ray diffraction patterns of zirconia-10 mol% scandia powders synthesized by the polyacrylamide technique (top) and the polymeric precursor (bottom) techniques.

agglomerates of diameter around 10 μm and exhibit regular spherical shapes. These agglomerates are not sintered due to the low energy environment during the thermal decomposition of small contents of organic compounds used in the synthetic route. These particles consist mainly of aggregates due to the weak Van der Waals forces. Scanning electron microscopy micrographs of fractured sintered pellets show that the Tosoh specimens are fully dense, the pellets prepared by the polymeric precursor technique are highly porous with irregular-shapes grains and the pellets prepared by the polyacrylamide technique have intergranular and intragranular pores with regular-shaped grains. All sintered pellets have an average grain size of <1 μm.

X-ray diffraction patterns of sintered pellets of zirconia-10 mol% scandia, using powders synthesized by the polyacrylamide and the polymeric precursor techniques, are presented in Fig. 2. The average crystallite size of both specimens determined using the Scherrer equation is ~5–8 nm, close to the value of the average particle size evaluated by BET measurements of surface area.

The Arrhenius plots of the bulk electrical resistivity of sintered pellets of ZrO_2:10 mol% Sc_2O_3 prepared by the polyacrylamide technique and by the polymeric precursor techniques are shown in Fig. 3. Results of commercial zirconia-8 mol% yttria are also shown for comparison purposes. The inset shows impedance spectroscopy diagrams of the three pellets measured at 408 °C. The zirconia-scandia pellet prepared using powders synthesized by the polyacrylamide technique has a lower value of the bulk electrical resistivity than the pellet prepared using the powders obtained by the polymeric precursor technique. One of the reasons is that the latter is less dense due to the higher content of organic residues in the powders than the former, and would require long term burning under oxygen to remove them. This is another advantage of the polyacrylamide
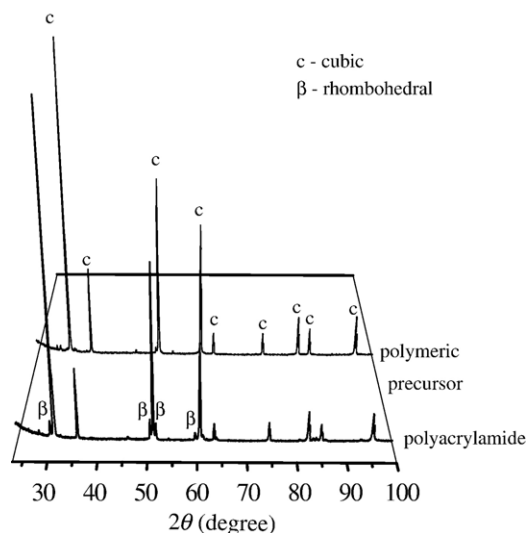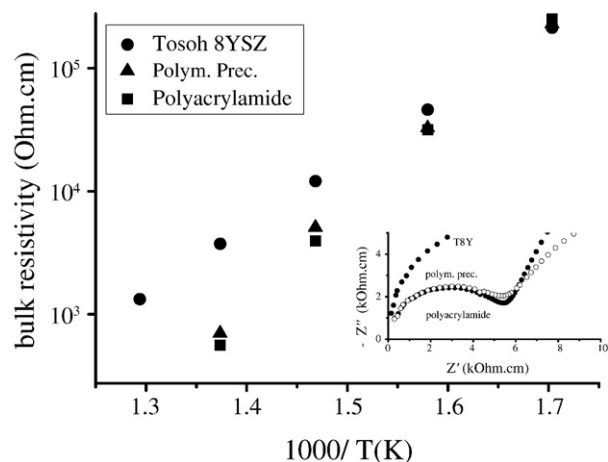

Fig. 3. Arrhenius plots of the bulk electrical resistivity of sintered pellets using powders synthesized by the polyacrylamide and the polymeric precursor techniques. Data of pellets using Tosoh T8Y are also shown. Inset: impedance spectroscopy diagrams of the sintered pellets, measured at 408 °C.

technique: simple calcination in air reduces to a larger extent the organic residues.

4. Conclusions

We have reported in detail the procedure to prepare nanosized $(ZrO_2)_{0.90}–(Sc_2O_3)_{0.10}$ powders by the polyacrylamide technique. A high value of average specific surface area was obtained, 78 m^2/g. The nanosized particles are single crystalline, the average particle size is 13 nm and the average value of the crystallite size is 5 nm. The technique is fast in comparison with other reported chemical techniques. Another advantage is that before calcination for obtaining the powders, the gel may be stored without degradation. Moreover, sintered pellets prepared with powders synthesized by the polyacrylamide technique have higher oxide ion conductivity than pellets prepared by the polymeric precursor technique.

Acknowledgments

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Fig. 2. X-ray diffraction patterns of ZrO_2: 10 mol% Sc_2O_3 pellets using powders synthesized by the polyacrylamide technique and by the polymeric precursor technique.

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